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Further Studies on Dislocations in Ferroelectric GASH Crystal

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Dislocation etch pits on *a*- or *b*-face of ferroelectric GASH crystal was studied. Spacial distribution of dislocation lines in GASH crystals was studied by continuous observation of dissolution process of *a*- or *b*-face and *c*-face. Dislocation which makes very small angle with *c*-plane causes a pit that accompanies a "wave front" of dissolution. Electron microscopic study of the pit was made and mechanism of etch pit formation is discussed.

§1 Introduction

The domain wall movement in ferroelectric crystals is believed to be governed by structure sensitive factors, and is shown to have interesting interactions with crystal imperfections especially with dislocations.[1] However, informations on dislocations in ferroelectric crystals are quite a few.

Etch pits on cleavage surface (i. e. {0001} face) of ferroelectric GASH crystal (guanidinium aluminum sulfate hexahydrate) have been identified with dislocation emergence points by one of the present authors.[2] On the other hand, observation of etch pits on *a*- or *b*-faces also concluded that they correspond to dislocation emergence points by the present authors, of which short communication has been published elsewhere.[3] Informations on both {0001} face and *a*- or *b*-face enable one to pursue the spacial distribution of dislocation lines, by observing continuously the process of dissolution which takes place preferentially at dislocation emergence points.

Present article firstly gives more detailed description of the results of study of dislocation etch pits on *a*- or *b*-face, than the previous short communication. Secondly it describes further works on dislocation etch pits, concerning spacial distribution of dislocation lines. Thirdly, some results of electronmicroscopic study are shown, which may give some informations on mechanism of pit formation or process of dissolution.

Crystallographic description of GASH was made by Wood,[4] reporting that space group is $P\text{-}31m$, and a-axis of the crystal is the normal of an edge of a triangular etch pit on (0001) face, while b-axis is the normal of an edge of an etch pit on $(000\bar{1})$ face, which is related to that on (0001) by two-fold axis normal to the a-axis. Cleavage of GASH crystal parallel to {0001} is complete.

§2 Dislocation Etch Pits on *a*- or *b*-Face

§2.1 Experimental Technique

The preparation of crystals are the same as before,[2] and crystals obtained are of hexagonal prismatic form, having edges of hexagon of a few cm and height of several millimeters. The a- or b-plate crystals were cut from as grown crystal by means of the wet thread, so as to be 1~3 mm thick. These crystals were etched by distilled water under a microscope. Surface of the crystal cut by the wet thread is rather irregular. By the etching, however, the surface is smoothed out. The etch pit can be fixed by drying on a kind of blotting paper, but during the drying process rough appearance of a surface sometimes cannot be avoided. Although etching rate can be slowed down by using a mixture of water and alcohol as an etchant, which has been used on cleavage faces, pit becomes much poorly detectable. Continuous observation of dissolution process provides the best technique to trace the dislocation lines, since the water acts not only as an etchant which attacks the stressed region around the emergence point of dislocations causing preferential etching but also it acts as a chemical polisher. It is advantageous that during the continuous observation rough surface never appears.

§2.2 Experimental Results

a) *Etch Pits*

Fig. 1 shows typical etch pits on a- or b-face. Longer sides of the etch pit are of the order of 50 μ and shorter sides 20 μ. An etch pit has qudruangular pyramidal form, and the deepness is of the order of a few microns. The deepest point displaces by a certain amount from the center of the periphery of etch pit. The displacement of the deepest point on a-face is towards (0001) face and that on b-face is towards $(000\bar{1})$ face. This assymmetry of the

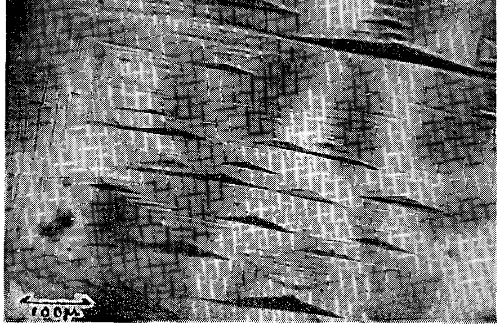


Fig. 1. Typical dislocation etch pits on a- or b-face.

shape of the etch pit is accompanied by every pit and is due to crystal symmetry, since experiments show that even the pit which corresponds to the emergence point of a dislocation running perpendicularly to the surface of the crystal is assymmetric.

b) *Pursuing Dislocation Lines*

By the continuous observation of the dissolution process of *a*- or *b*-cut GASH crystals, dislocation lines are traced to a certain extent. In the dissolution process of the crystals, etch pits stay at certain sites, until the water is saturated and the dissolution ceases. When the water has been saturated, etch pits become undetectable. In a subsequent addition of a water drop, dissolution takes place again, and etch pits are formed at the same sites as before. An example of this phenomehon is shown in Fig. 2.

Crystals are fixed on a slide glass using a certain kind of adhesive and only one surface is carefully etched, followed by drying. Dislocations are followed, measuring chemically polished distance by a dial of microscope, of which one division corresponds to 2 μ. Fig. 3 contains a series of photomicographs taken in the sequence of the above treatment. All the etch pits on the surface of Fig. 3d perfectly correspond to the pits included in Fig. 3a, although the chemically polished distance reaches even about 100 μ. A map of dislocation lines can be constructed. The projection on *a*-*b*-plane (Fig. 3e) shows that some

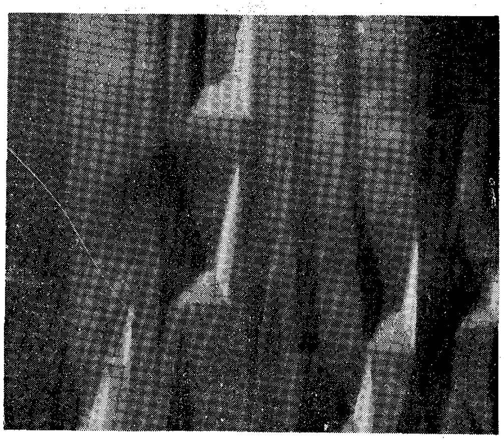


Fig. 2a. Surface of crystal is covered by a solution nearly saturated. Pits are rather difficult to detect.

Fig. 2b. Solution which covers the surface of the crystal has been saturated, and the dissolution does not take place any more.

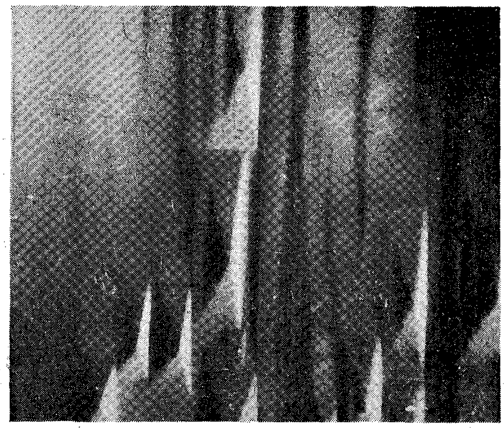
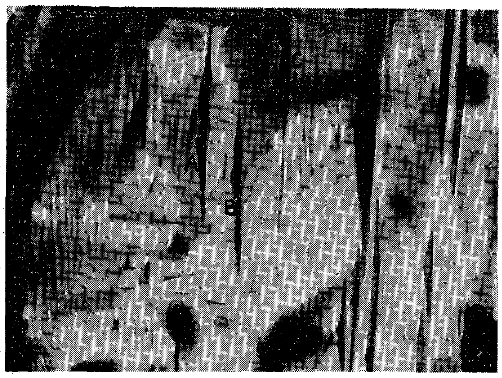
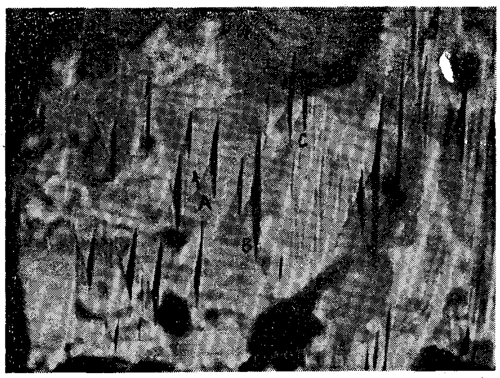


Fig. 2c. Immediately after a subsequent addition of a water drop, preferential dissolution at dislocation emergence points has started, and pits are sharply detected.

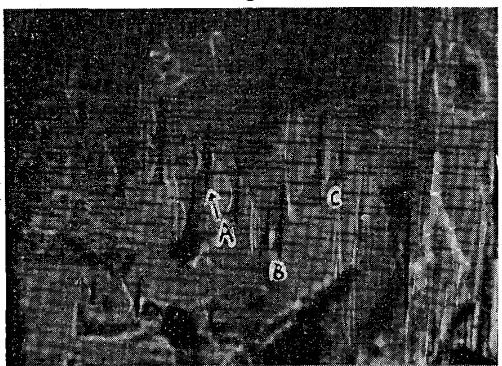


a

b



c



d

Fig. 3a, b, c and d. Photomicrographs of *a*- or *b*-face, which has been dissolved a certain distance and dried. b, c, and d correspond to 15 μ, 45 μ and 105 μ below the initial face a.

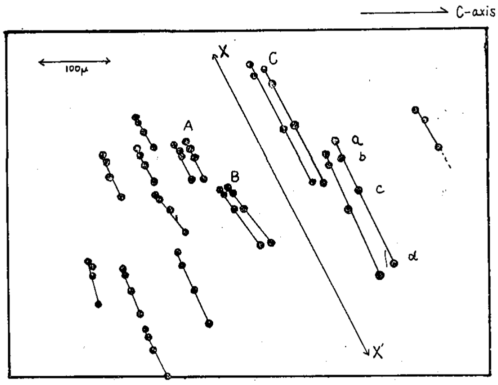


Fig. 3e. Projection of dislocation lines on *a*- or *b*-plane.

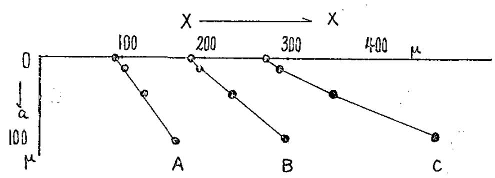


Fig. 3f. Projection of three nearly parallel dislocation lines on the plane, which is defined by *a*-axis and XX′.

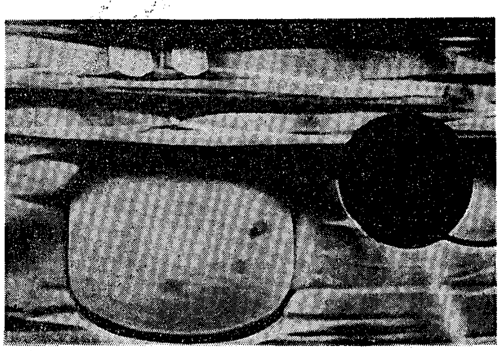


Fig. 4. Penetrating dissolution along dislocation lines.

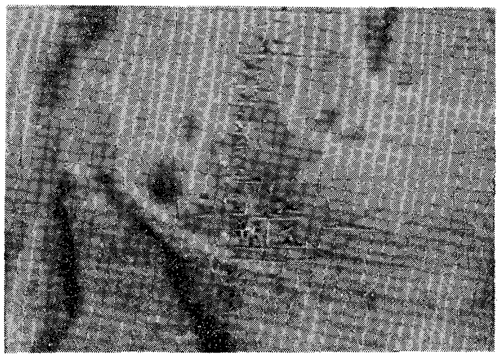


Fig. 5. Small angle tilt boundary.

dislocation lines are nearly parallel to each other. Projection of three nearly parallel dislocation lines on the plane, which is determined by a-axis and XX′, is shown in Fig. 3f. Since the accuracy of the measurement of the chemically polished distance is not sufficient, some parts of lines in Fig. 3f must be elongated or shortened in the a-or b-direction, to obtain true shape of the dislocation lines. But it will be concluded, that the dislocation lines in Fig. 3f make rather small angles with a- or b-face.

c) *Penetrating Dissolution*

When the dissolution process of a thin a- or b- plate crystal is observed continuously, preferential dissolution takes place at the emergence points of dislocations on the top and the bottom surfaces of the crystal, until the "penetrating dissolution" results along the dislocations. Fig. 4 is a photomicrograph of the thin crystal, immediately after the penetrating dissolution has taken place.

Observation of the penetrating dissolution provides one of conclusive evidences for the observed pits to correspond to emergence points of dislocations on the crystal surface.

d) *Grain Boundary*

Linear array of etch pits as shown in Fig. 5 is sometimes observed. This array is conceived of small angle tilt boundary. Tilt angle is, for Fig. 5, estimated to be

$$\tan\theta = 6.6\times 10^{-5}.$$

e) *Pit Density*

Density of etch pits was conunted over 20 photomicrographs. Distribution curve is shown in Fig. 6, which indicates that the pit

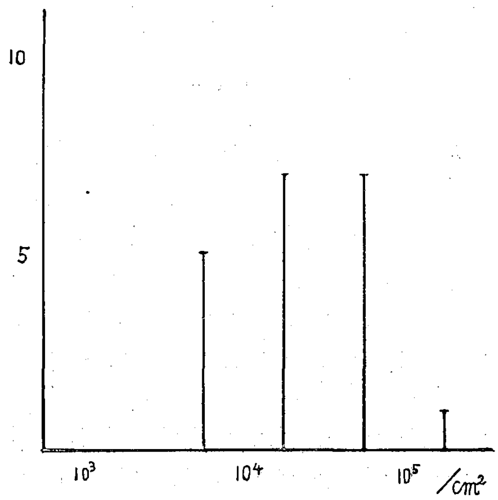


Fig. 6. Distribution of density of pits observed on a- or b-face.

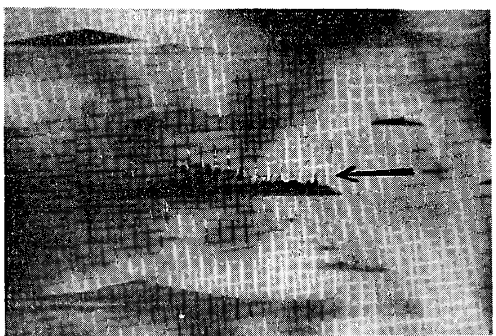


Fig. 7. Photomicrograph of dislocation etch pits produced by mechanical shock. A group of small pits shown by an arrow is the pits produced by the mechanical shock, while large pits have remained to exist before the shock is given.

density on *a*- or *b*-surface is of the same order or a little higher than on the cleavage face. The geometrical mean was calculated to be $1.8 \times 10^4/cm^2$. while on cleavage face $0.7 \times 10^4/cm^2$.[2)]

f) Production of Etch Pits by Mechanical Stresses

Dissolution Process of the *a*- or *b*-face of the crystal is observed continuously, and mechanical shock is given by a contact of point of a needle. A group of small etch pits is produced by the shock, as shown by an arrow in Fig. 7. These pits are conceived to correspond to dislocations produced by the mechanical shock.

§3 Studies of Etch Pits on Cleavage Surface

§3.1 Experimental Technique

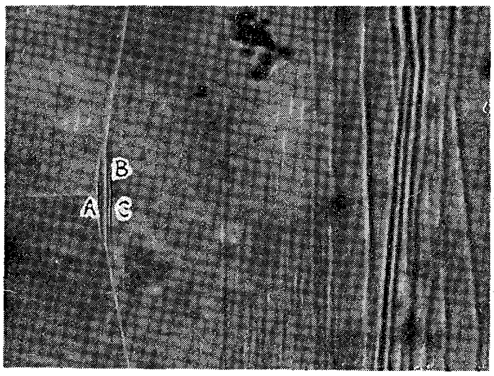
To inquire the spacial distribution of dislocation lines, two methods were tried. The first method consists in that a few mm thick crystal is cloven into several thin pieces, a few hundreds micron of thickness, and every cleavage surface undergoes etching treatment. The second method is to follow the dislocation lines by observing the dissolution process of cleavage face continuously. Dissolution of GASH crystal takes place by nucleation and progression of steps, of which aspects will be reported elsewhere.[5)] Nucleation of the steps cccurs at crystal edges and at dislocation emergence points.

§3.2 Experimental Results

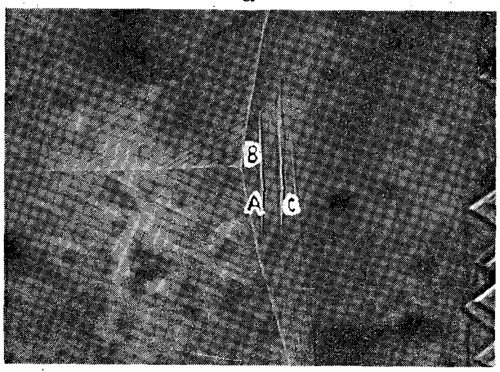
From experiments described in §3.1, that trace dislocation lines, and from results of §2, following conclusions can be drawn. Some dislocation lines are parallel to *c*- direction, but there is no special directions, to one of which any dislocation line is parallel, and there is no special planes, in one of which any dislocation line lies. Some dislocation lines run obliquely to the *c*-face. Even dislocation lines which make extremely low angle with the *c*-surface are observed. Some dislocations can be followed for about a few hundred microns, but some make loops before reaching 100 μ.

The above result is reasonable because the dislocations studied are only those which have been generated in the process of crystal growth.

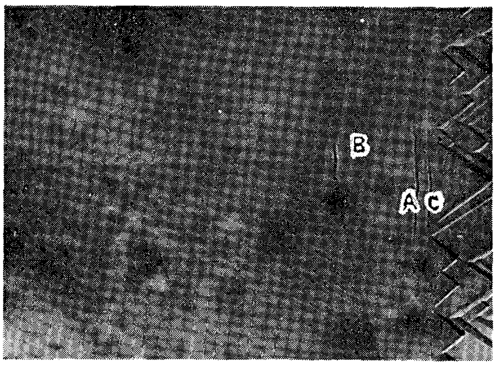
Fig. 8 contains an example of photomicrographs obtained by the second method which has been mentioned above in §3.1. The dislocations which make extremely small angles with *c*-face are caught. A and C among three dislocation lines are easily seen to be almost



a



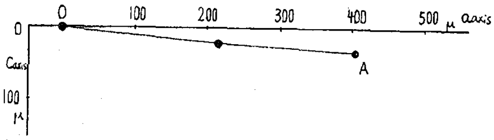
b



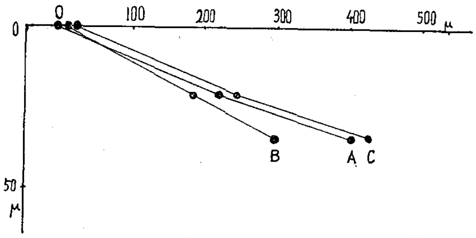
c

Fig. 8. Persuing dislocation lines which make very small angles with {0001} face.

b and c correspond to the surfaces 20 μ and 52 μ lower than the initial surface a.



d



e

Fig. 8d. Projection of the dislocation A on *a*-*c*-plane.

Fig. 8e. Projection of three dislocations on *a*-*c*-plane, scale of *c*-direction being enlarged.

parallel to each other, because distance between their emergence points remains almost constant during dissolution process (Fig. 8a, b and c). Another dislocation B makes a little larger angle with *c*- plane, hence its emergence point is overtaken by A and remains behind. Fig. 8d is projection of the dislocation A on *a*-*c*-plane, while Fig. 8e is that of three dislocations, scale of *c*-direction being enlarged.

It will be noticed that emergence points of dislocations in Fig. 8a, b and c accompany something like "wave front" of rather peculiar shape. Only for a dislocation which makes extremely small angle with *c*-face, the "wave front" is expected, since the region around *P* in Fig. 9c may be more soluble than the part far from it, or the solubility will be a decreasing function or *r*, where *r* denotes the distance from the dislocation. For a dislocation perpendicular or somewhat inclined to *c*-face, the "wave front" is not expected (Fig. 8a and b).

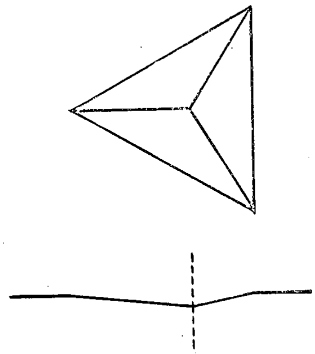


Fig. 9a. Dislocation perpendicular to {0001} face.

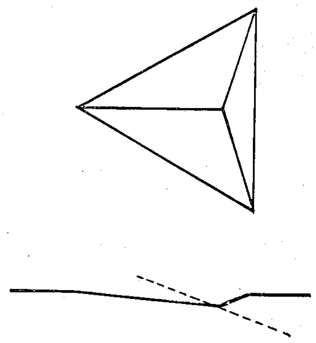


Fig. 9b. Dislocation which makes a certain angle with {0001} face.

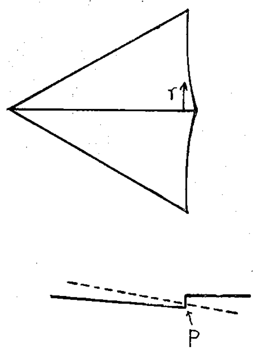


Fig. 9c. Dislocation which makes very small angle with {0001} face.

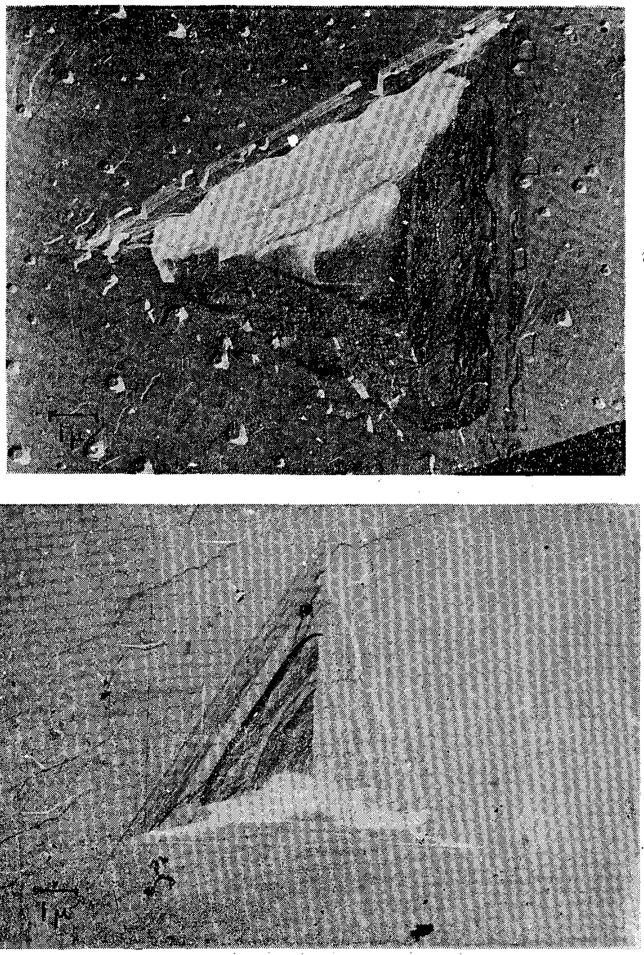
§4 Electronmicroscopic Study of Etch Pits

Etch pits on cleavage face were observed by an electronmicroscope. As GASH crystal is very easily soluble in water, direct reprica method can be used. A cleavage face of GASH crystal is etched by a certain mixture of alcohol and water, triangular etch pits being obtained. Carbon is deposited on this sample, followed by shadowing by means of chromium. When this sample is put in water, GASH crystal is dissolved out, and only the reprica rises up to the surface of the water. Since the etch pit is rather shallow,[2] low angle shadowing of about 0.1 radians is required.

Typical electronmicrographs are shown in Fig. 10. Fig. 10a corresponds to a dislocation perpendicular to the cleavage face, while b corresponds to one not perpendicular.

The typical etch pit consists of (1) part of periphery, which is composed of an assembly of steps, (2) middle part, which is a slope of several degrees, with a few steps, and (3) bottom part, which is not sharp but round, although it seems sharply pointed by optical observation. The existence of steps in the periphery part is what makes the dislocation etch pits on *c*-face well-marked and makes the observation easy. The preference of step formation is a characteristic behavior of *c*-face of GASH, as can be seen from the observation of dissolution process of *c*-face.[5] This characteristic behavior is rather lacking on *a*- or *b*-face, providing the reason why the etch pit is less well-marked on *a*- or *b*-face.

The mechanism of the etch pit formation will be roughly as follows. Around a dislocation line there is a stress field which dies off as $1/r$, where r is a distance from the dislocation. Elastic energy of a unit volume near the dislocation is



a

b

Fig. 10. Eelectronmicrograph of etch pit on {0001} face.
a corresponds to a dislocation perpendicular to the surface.
b corresponds to a dislocation not perpendicular to the surface.

$$\varepsilon \doteqdot \varepsilon\left(\frac{1}{r^2}\right) \quad .$$

If a pit is formed at the emergence point of dislocation, at the expence of surface energy increase, the net energy change is

$$\delta F = -\int \varepsilon\left(\frac{1}{r^2}\right) dV + \int \sigma dS \quad ,$$

where $\int \sigma dS$ denotes the increase of surface energy. Since the decrease of elastic energy is integrated by volume, and the increase of surface energy is integrated by the surface area, resultant energy increment will be as Fig. 11. A pit that cor-

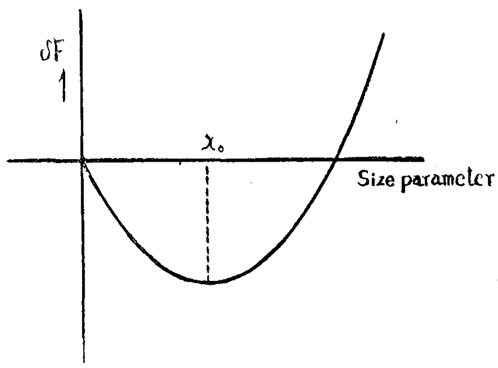


Fig. 11. Qualititative curve for energy change due to pit formation.

responds to the minimum of δF curve is first formed, and then it grows if undersaturated solvent is supplied. In the growing process, shape change of the pit takes place, and steps are formed. As mentioned above, *c*-face of GASH crystal has the characteristic behavior that the steps are easily formed,[5] some steps will be formed at the periphery and some on the slope. Observed shape of etch pits seems to show that this mechanism is essentially the case.

In Fig. 10 a round hillocks are observed. These hillocks have nothing to do with dislocations, but may be formed depending on the surface conditions. This hillock was able to be ensured not to be pit but hillock, only by the electronmicroscopic study.

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